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Crystal structure of 5,17-bis(*N-tert*-butylhydroxyamine)-11,23-dibromo-25,26,27,28-tetrapropoxycalix[4]arene, $C_{48}H_{64}Br_2N_2O_6$

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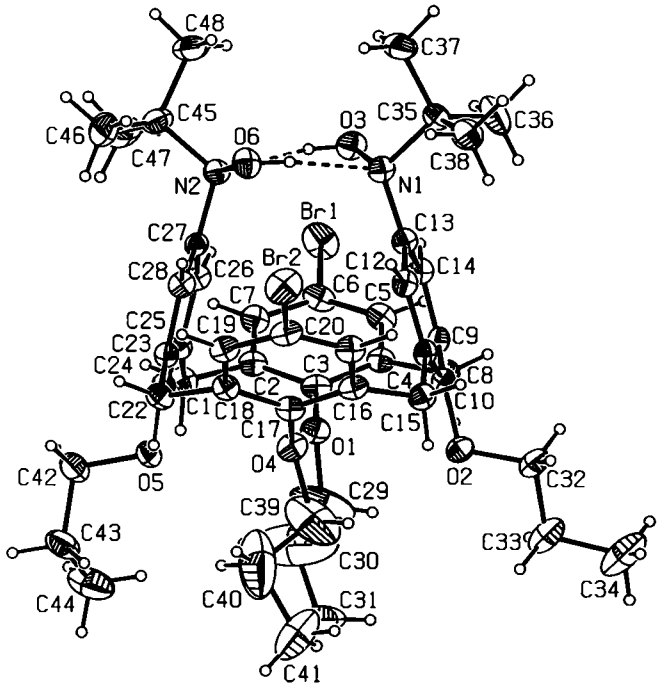

Abstract

$C_{48}H_{64}Br_2N_2O_6$, monoclinic, $P12_1/c1$ (no. 14), a = 13.935(3) Å, b = 20.589(3) Å, c = 17.349(4) Å, β = 99.09(2)°, V = 4915.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.070, $wR_{ref}(F^2)$ = 0.149, T = 295 K.

Source of material

The title compound was prepared starting from the precursor compound 5,11,17,23-tetrabromo-25,26,27,28-tetrapropoxycalix[4]arene, which was obtained according to [1], in a similar one-step procedure as described in [2] and recrystallized from chloroform/methanol.

Discussion

Calixarenes are cavity-containing macrocyclic compounds made up of substituted phenols with aldehydes [3]. Investigations of spin exchange interaction between nitroxide spin centers on the low rims of calixarene have been already performed [4,5]. One of us firstly reported the synthesis of a kind of paramagnetic calix[4]arene with *N-tert*-butyl nitroxide on the upper rims and the study on spin exchange interactions [2]. The calixarene derivatives with *N-tert*-butylhydroxyamine groups constitute valuable precursors for this kind of paramagnetic calixarene. As a part of our ongoing investigations of the preparation of paramagnetic calix[4]arene, we recently synthesized another calix[4]arene derivative with *N-tert*-butylhydroxyamine groups on the upper rims.

The molecule in the crystal structure of the title compound displays non-crystallographic twofold symmetry. The cone conformation of the calix[4]arene cavity is retained from the precursor, but pinched due to the two O–H···N hydrogen bonds between the two *N-tert*-butylhydroxyamine groups on the upper rims. The hydrogen bond lengths are 2.07 Å for H3A···N2 and 2.04 Å for H6A···N1, and the angles are 150.8° for ∠O3–H3A···N2 and 151.9° for ∠O6–H6A···N1. The two dihedral angles are 75.5° for the phenyl ring C9 – C14 and 146.0° for the phenyl ring C2 – C7 to the reference plane of the bridging C atoms (here C1, C8 and their equivalents). The distances between centroids for the two symmetry-equivalent phenyl rings are 4.60 Å for ring C9 – C14 and its equivalent, and 7.78 Å for ring C2 – C7 and its equivalent.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.1 × 0.4 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.95 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9049, 8671
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3589
$N(param)_{refined}$:	525
Program:	SHELXTL [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3A)	4e	0.4656	0.3276	0.7324	0.104
H(6A)	4e	0.4693	0.4363	0.7727	0.104
H(1A)	4e	0.7914	0.2070	0.9069	0.070
H(1B)	4e	0.8761	0.2460	0.8785	0.070
H(5A)	4e	0.6684	0.1678	0.5846	0.074
H(7A)	4e	0.7026	0.1341	0.8147	0.074
H(8A)	4e	0.7266	0.2657	0.5331	0.069
H(8B)	4e	0.8255	0.2918	0.5788	0.069
H(12A)	4e	0.5984	0.4924	0.6744	0.066
H(14A)	4e	0.5787	0.3069	0.6094	0.065
H(15A)	4e	0.8445	0.5154	0.6477	0.074
H(15B)	4e	0.7519	0.5558	0.6139	0.074
H(19A)	4e	0.7171	0.5917	0.9291	0.074
H(21A)	4e	0.6871	0.6277	0.7006	0.076
H(22A)	4e	0.7975	0.4977	0.9862	0.072
H(22B)	4e	0.8845	0.4715	0.9475	0.072

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(26A)	4e	0.6212	0.2714	0.8386	0.064
H(28A)	4e	0.6279	0.4579	0.9023	0.068
H(29A)	4e	0.9610	0.3016	0.6775	0.237
H(29B)	4e	0.9867	0.3351	0.7578	0.237
H(30A)	4e	0.9983	0.2066	0.7322	0.462
H(30B)	4e	1.0260	0.2414	0.8134	0.462
H(31A)	4e	1.1650	0.2312	0.7537	0.305
H(31B)	4e	1.1408	0.3051	0.7618	0.305
H(31C)	4e	1.1134	0.2701	0.6810	0.305
H(32A)	4e	0.8532	0.4665	0.5032	0.089
H(32B)	4e	0.8127	0.3968	0.4792	0.089
H(33A)	4e	1.0114	0.4229	0.5362	0.131
H(33B)	4e	0.9711	0.3534	0.5122	0.131
H(34A)	4e	1.0417	0.3975	0.4112	0.246
H(34B)	4e	0.9716	0.4574	0.4068	0.246
H(34C)	4e	0.9301	0.3883	0.3826	0.246
H(36A)	4e	0.4439	0.3789	0.5070	0.171
H(36B)	4e	0.3307	0.3877	0.4917	0.171
H(36C)	4e	0.3775	0.3303	0.5439	0.171
H(37A)	4e	0.3046	0.4413	0.6832	0.150
H(37B)	4e	0.2908	0.3693	0.6541	0.150
H(37C)	4e	0.2448	0.4264	0.6008	0.150
H(38A)	4e	0.4101	0.5157	0.6262	0.140
H(38B)	4e	0.3547	0.5027	0.5417	0.140

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(38C)	4e	0.4675	0.4927	0.5604	0.140
H(39A)	4e	0.9915	0.4420	0.7458	0.244
H(39B)	4e	0.9643	0.5158	0.7416	0.244
H(40A)	4e	1.0447	0.4515	0.8750	0.341
H(40B)	4e	1.0183	0.5264	0.8700	0.341
H(41A)	4e	1.1809	0.5136	0.8426	0.345
H(41B)	4e	1.1145	0.5383	0.7669	0.345
H(41C)	4e	1.1431	0.4647	0.7754	0.345
H(42A)	4e	0.9145	0.2986	1.0286	0.100
H(42B)	4e	0.9064	0.3732	1.0459	0.100
H(43A)	4e	1.0635	0.3428	1.0902	0.117
H(43B)	4e	1.0644	0.3883	1.0180	0.117
H(44A)	4e	1.1671	0.3013	1.0101	0.219
H(44B)	4e	1.0810	0.2976	0.9402	0.219
H(44C)	4e	1.0815	0.2524	1.0130	0.219
H(46A)	4e	0.4383	0.4405	0.9541	0.163
H(46B)	4e	0.5233	0.3969	0.9956	0.163
H(46C)	4e	0.4166	0.3847	1.0104	0.163
H(47A)	4e	0.5309	0.2800	0.9590	0.175
H(47B)	4e	0.4600	0.2525	0.8872	0.175
H(47C)	4e	0.4216	0.2672	0.9656	0.175
H(48A)	4e	0.3170	0.3950	0.8461	0.168
H(48B)	4e	0.2925	0.3365	0.8975	0.168
H(48C)	4e	0.3279	0.3235	0.8175	0.168

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4e	0.60577(7)	0.06446(4)	0.67954(5)	0.1186(8)	0.0583(5)	0.1171(7)	−0.0308(5)	−0.0110(6)	0.0068(5)
Br(2)	4e	0.62906(7)	0.69711(4)	0.83019(5)	0.1168(7)	0.0591(5)	0.1262(8)	0.0271(5)	0.0381(6)	0.0017(5)
O(1)	4e	0.8546(3)	0.3032(2)	0.7368(2)	0.063(3)	0.052(3)	0.077(3)	−0.011(3)	0.007(3)	−0.003(2)
O(2)	4e	0.8542(3)	0.4070(2)	0.5937(2)	0.063(3)	0.054(3)	0.068(3)	−0.003(2)	0.020(3)	0.001(2)
O(3)	4e	0.4552(3)	0.3318(2)	0.6848(3)	0.073(3)	0.053(3)	0.083(3)	−0.010(2)	0.013(3)	0.006(2)
O(4)	4e	0.8696(4)	0.4615(2)	0.7905(3)	0.073(3)	0.052(3)	0.083(3)	0.007(3)	0.022(3)	−0.002(2)
O(5)	4e	0.9063(3)	0.3538(2)	0.9335(2)	0.060(3)	0.058(3)	0.057(3)	0.002(2)	−0.001(2)	0.007(2)
O(6)	4e	0.4766(3)	0.4331(2)	0.8204(2)	0.078(3)	0.055(3)	0.072(3)	0.017(2)	0.007(3)	0.010(2)
N(1)	4e	0.4747(4)	0.3989(2)	0.6643(3)	0.061(4)	0.042(3)	0.067(4)	−0.003(3)	0.012(3)	0.005(3)
N(2)	4e	0.5023(4)	0.3664(2)	0.8432(3)	0.053(4)	0.050(3)	0.064(4)	0.006(3)	0.007(3)	0.013(3)
C(1)	4e	0.8064(5)	0.2391(3)	0.8697(3)	0.068(5)	0.045(4)	0.061(5)	0.011(4)	0.003(4)	0.002(3)
C(2)	4e	0.7751(5)	0.2139(3)	0.7877(4)	0.055(4)	0.037(4)	0.072(5)	0.009(3)	0.011(4)	−0.001(4)
C(3)	4e	0.7964(4)	0.2491(3)	0.7236(4)	0.050(4)	0.030(4)	0.081(5)	0.004(3)	0.012(4)	−0.006(4)
C(4)	4e	0.7515(4)	0.2348(3)	0.6476(4)	0.052(4)	0.041(4)	0.067(5)	0.011(3)	0.011(4)	−0.006(4)
C(5)	4e	0.6956(5)	0.1795(3)	0.6351(4)	0.067(5)	0.038(4)	0.076(5)	0.007(4)	−0.001(4)	−0.001(4)
C(6)	4e	0.6799(5)	0.1417(3)	0.6971(5)	0.063(5)	0.034(4)	0.094(6)	−0.004(3)	−0.006(4)	0.001(4)
C(7)	4e	0.7168(5)	0.1591(3)	0.7733(4)	0.070(5)	0.041(4)	0.073(5)	0.006(4)	0.008(4)	0.011(4)
C(8)	4e	0.7580(5)	0.2833(3)	0.5826(3)	0.069(5)	0.049(4)	0.056(4)	0.002(4)	0.013(4)	−0.011(3)
C(9)	4e	0.7079(5)	0.3461(3)	0.6005(3)	0.063(5)	0.047(4)	0.042(4)	−0.002(4)	0.010(3)	0.003(3)
C(10)	4e	0.7589(5)	0.4050(3)	0.6076(3)	0.050(5)	0.059(5)	0.049(4)	0.001(4)	0.011(3)	0.005(3)
C(11)	4e	0.7194(5)	0.4607(3)	0.6357(3)	0.062(5)	0.040(4)	0.048(4)	−0.006(3)	0.010(3)	0.007(3)
C(12)	4e	0.6254(5)	0.4563(3)	0.6538(3)	0.068(5)	0.040(4)	0.057(4)	0.009(4)	0.012(4)	0.004(3)
C(13)	4e	0.5709(5)	0.3999(3)	0.6421(3)	0.059(5)	0.038(4)	0.057(4)	−0.002(4)	0.009(4)	0.004(3)
C(14)	4e	0.6141(5)	0.3453(3)	0.6163(3)	0.061(5)	0.046(4)	0.055(4)	−0.002(4)	0.009(4)	−0.001(3)
C(15)	4e	0.7770(5)	0.5233(3)	0.6523(4)	0.069(5)	0.049(4)	0.069(5)	−0.006(4)	0.015(4)	0.009(4)
C(16)	4e	0.7711(5)	0.5487(3)	0.7328(4)	0.056(4)	0.034(4)	0.076(5)	−0.009(3)	0.017(4)	−0.007(4)
C(17)	4e	0.8121(5)	0.5142(3)	0.7993(4)	0.058(5)	0.031(4)	0.074(5)	−0.005(3)	0.010(4)	−0.010(4)
C(18)	4e	0.7896(5)	0.5273(3)	0.8721(4)	0.061(5)	0.038(4)	0.062(5)	−0.011(3)	0.005(4)	−0.005(4)
C(19)	4e	0.7327(5)	0.5814(3)	0.8804(4)	0.065(5)	0.047(4)	0.077(5)	−0.009(4)	0.017(4)	−0.007(4)
C(20)	4e	0.6993(5)	0.6197(3)	0.8169(5)	0.060(5)	0.039(4)	0.091(6)	−0.005(3)	0.022(4)	−0.011(4)
C(21)	4e	0.7145(5)	0.6030(3)	0.7434(4)	0.067(5)	0.041(4)	0.081(5)	−0.002(4)	0.013(4)	0.004(4)
C(22)	4e	0.8151(4)	0.4796(3)	0.9388(4)	0.060(4)	0.049(4)	0.066(5)	−0.005(3)	−0.002(4)	−0.003(4)
C(23)	4e	0.7600(5)	0.4162(3)	0.9183(3)	0.056(5)	0.045(4)	0.049(4)	−0.006(3)	0.007(3)	−0.003(3)
C(24)	4e	0.8060(4)	0.3567(3)	0.9128(3)	0.041(4)	0.050(4)	0.048(4)	0.006(3)	0.003(3)	0.009(3)
C(25)	4e	0.7557(5)	0.3021(3)	0.8827(3)	0.052(4)	0.044(4)	0.050(4)	0.005(4)	0.008(3)	0.008(3)
C(26)	4e	0.6559(5)	0.3073(3)	0.8603(3)	0.059(5)	0.039(4)	0.061(4)	−0.001(3)	0.011(4)	−0.002(3)
C(27)	4e	0.6059(5)	0.3650(3)	0.8694(3)	0.048(4)	0.048(4)	0.051(4)	0.002(4)	0.011(3)	0.009(3)
C(28)	4e	0.6598(5)	0.4188(3)	0.8974(3)	0.063(5)	0.045(4)	0.065(5)	0.001(4)	0.015(4)	−0.002(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(29)	4*e*	0.9569(6)	0.2965(5)	0.7324(9)	0.11(1)	0.080(8)	0.37(2)	–0.033(7)	–0.07(1)	0.01(1)
C(30)	4*e*	1.0210(9)	0.2471(7)	0.757(1)	0.17(2)	0.35(3)	0.65(5)	–0.04(2)	0.10(2)	–0.18(3)
C(31)	4*e*	1.1190(6)	0.2650(7)	0.7366(7)	0.062(7)	0.33(2)	0.22(1)	–0.013(9)	0.031(8)	–0.07(1)
C(32)	4*e*	0.8621(5)	0.4205(3)	0.5138(4)	0.078(6)	0.075(5)	0.078(6)	–0.017(4)	0.035(4)	–0.008(4)
C(33)	4*e*	0.9628(6)	0.3993(4)	0.5007(5)	0.123(8)	0.107(7)	0.114(7)	–0.019(6)	0.069(6)	–0.008(6)
C(34)	4*e*	0.9780(7)	0.4117(5)	0.4178(5)	0.19(1)	0.15(1)	0.18(1)	–0.060(8)	0.129(9)	–0.047(8)
C(35)	4*e*	0.3921(5)	0.4184(4)	0.6023(4)	0.057(5)	0.085(6)	0.066(5)	0.012(4)	0.000(4)	0.011(4)
C(36)	4*e*	0.3854(6)	0.3747(4)	0.5293(4)	0.126(8)	0.134(8)	0.069(6)	0.029(6)	–0.027(5)	–0.019(5)
C(37)	4*e*	0.2995(5)	0.4134(4)	0.6385(5)	0.058(5)	0.126(7)	0.112(7)	0.007(5)	0.004(5)	0.023(6)
C(38)	4*e*	0.4075(5)	0.4889(4)	0.5807(4)	0.083(6)	0.098(6)	0.098(6)	0.029(5)	0.009(5)	0.035(5)
C(39)	4*e*	0.9685(7)	0.4776(5)	0.7746(8)	0.19(1)	0.16(1)	0.24(2)	0.12(1)	–0.05(1)	–0.07(1)
C(40)	4*e*	1.036(1)	0.4891(8)	0.8410(7)	0.42(3)	0.32(2)	0.11(1)	0.14(2)	0.04(2)	–0.00(1)
C(41)	4*e*	1.1273(9)	0.5027(7)	0.8029(8)	0.25(2)	0.28(2)	0.19(1)	–0.02(1)	0.14(1)	0.03(1)
C(42)	4*e*	0.9358(5)	0.3415(4)	1.0155(4)	0.075(6)	0.088(6)	0.079(6)	–0.008(4)	–0.012(4)	0.015(4)
C(43)	4*e*	1.0444(5)	0.3459(4)	1.0340(5)	0.069(6)	0.109(7)	0.104(7)	–0.023(5)	–0.021(5)	0.015(5)
C(44)	4*e*	1.0984(6)	0.2947(5)	0.9958(6)	0.082(7)	0.16(1)	0.18(1)	0.027(7)	–0.016(7)	–0.031(8)
C(45)	4*e*	0.4400(5)	0.3502(4)	0.9037(5)	0.058(5)	0.085(6)	0.097(6)	0.007(4)	0.025(5)	0.031(5)
C(46)	4*e*	0.4560(6)	0.3975(4)	0.9723(4)	0.103(7)	0.157(9)	0.071(6)	0.023(6)	0.030(5)	–0.008(6)
C(47)	4*e*	0.4655(6)	0.2811(4)	0.9314(5)	0.091(6)	0.124(8)	0.142(8)	–0.004(6)	0.039(6)	0.069(6)
C(48)	4*e*	0.3345(5)	0.3514(4)	0.8623(5)	0.054(5)	0.158(9)	0.127(7)	0.001(5)	0.022(5)	0.039(6)

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